

DECLARATION

I, Kyoko HIROTA, c/o the Inoue & Associates of 3rd Floor, Akasaka Habitation Building, 3-5, Akasaka 1-chome, Minato-ku, Tokyo, Japan do solemnly and sincerely declare that I am conversant with the Japanese and English languages and that I have executed with the best of my ability this translation into English of the Certified Copy of Japanese Patent Application No. 2002-184808 and believe that the translation is true and correct.

The undersigned petitioner declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

October 14, 2009
(Date)

Kyoko Hirota
(Signature)

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[Name of Material] Specification 1

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[Title of the Invention] Photosensitive resin composition
for forming a laser engravable printing element and a laser
engravable printing element produced using the same

[Scope of Claims for Patent]

[Claim 1]

A photosensitive resin composition for forming a laser
engravable printing element, comprising:

- (a) a resin which is in a solid state at 20 °C,
- (b) an organic compound having a polymerizable unsaturated group, and
- (c) an inorganic porous material having a specific surface area of from 10 m²/g to 1,500 m²/g, an average pore diameter of from 1 nm to 1,000 nm, a pore volume of from 0.1 ml/g to 10 ml/g and an oil absorption value of from 10 ml/100 g to 2,000 ml/100 g.

[Claim 2]

The photosensitive resin composition according to claim 1, wherein said resin (a) which is in a solid state at 20 °C has a number average molecular weight of from 5,000 to 300,000 and said organic compound (b) having a polymerizable unsaturated group has a number average molecular weight of less than 5,000.

[Claim 3]

The photosensitive resin composition according to claim

1, wherein at least 30 % by weight of said resin (a), which is in a solid state at 20 °C, is at least one resin selected from the group consisting of a thermoplastic resin having a softening temperature of 500 °C or less and a solvent-soluble resin.

[Claim 4]

The photosensitive resin composition according to claim 1, wherein at least 20 % by weight of said organic compound (b) is a derivative of at least one compound selected from the group consisting of an alicyclic compound and an aromatic compound.

[Claim 5]

The photosensitive resin composition according to claim 1, wherein said inorganic porous material (c) has a number average particle diameter of from 0.1 μm to 100 μm .

[Claim 6]

A laser engravable printing element produced by a process comprising:

shaping the photosensitive resin composition of any one of claims 1 to 5 into a sheet or cylinder, and

crosslink-curing said photosensitive resin composition by light or electron beam irradiation.

[Claim 7]

A multi-layered, laser engravable printing element comprising a printing element layer and at least one elastomer

layer provided below the printing element layer, wherein said printing element layer is made of the laser engravable printing element of claim 6 and said elastomer layer has a Shore A hardness of from 20 to 70 and has a uniform thickness.

[Claim 8]

The multi-layered, laser engravable printing element according to claim 7, wherein said elastomer layer is formed by curing a photosensitive resin composition which is in a liquid state at room temperature.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention is concerned with a photosensitive resin composition which can be advantageously used for forming a relief pattern of a flexographic printing plate by laser engraving; a pattern for surface processing, such as embossing; and a relief pattern for printing tiles and the like. Further, the present invention is also concerned with a laser engravable printing element formed from the above-mentioned photosensitive resin composition.

[0002]

[Prior Art]

The flexographic printing method is used in the production of packaging materials (such as a cardboard, a paperware, a paper bag and a flexible packaging film) and materials for

construction and furnishing (such as a wall paper and an ornamental board) and also used for printing labels. Such flexographic printing method has been increasing its importance among other printing methods. A photosensitive resin is generally employed for producing a flexographic printing plate, and the production of a flexographic printing plate using a photosensitive resin has conventionally been performed by the following method. A photo-mask bearing a pattern is placed on a liquid resin or a solid resin sheet (obtained by molding a resin into a sheet), and the resultant masked resin is imagewise exposed to light, to thereby crosslink the exposed portions of the resin, followed by developing treatment in which the unexposed portions of the resin (i.e., uncrosslinked resin portions) are washed away with a developing liquid. Recently, the so-called "flexo CTP method" has been developed. In this method, a thin, light absorption layer called "black layer" is formed on the surface of a photosensitive resin plate, and the resultant resin plate is irradiated with a laser to form a mask bearing an image on the resin plate directly without separately preparing a mask. Subsequently, the resultant resin plate is imagewise exposed to light through the mask, to thereby crosslink the exposed portions of the resin, followed by developing treatment in which the unexposed portions of the resin (i.e., uncrosslinked resin portions) are washed away

with a developing liquid. Since the efficiency in producing the printing plates has been improved by this method, its use is beginning to expand in a wide variety of fields. However, this method also requires a developing treatment as in the case of other methods and, hence, the improvement in the efficiency in producing the printing plates is limited. Therefore, it has been desired to develop a method for forming a relief pattern directly on a printing element by using a laser without a need for a developing treatment.

[0003]

As an example of such method, there can be mentioned a method in which a printing element is engraved directly with a laser. This method has already been used for producing relief plates and stamps, in which various materials are used for forming the printing elements.

For example, U.S. Patent No. 3,549,733 discloses the use of a polyoxymethylene or polychloral for forming a printing element. Further, Japanese Patent Application prior-to-examination Publication (Tokuhyo) No. Hei 10-512823 (corresponding to DE 19625749 A) describes the use of a silicone polymer or a silicone fluoropolymer for forming a printing element. In each of the specific examples of compositions used for forming the printing element, which are described in this patent document, fillers, such as amorphous silica, are added to the above-mentioned polymer. However, a photo-

sensitive resin is not used in the inventions disclosed in the above-mentioned patent documents. In the above-mentioned Japanese Patent Application prior-to-examination Publication (Tokuhyo) No. Hei 10-512823, amorphous silica is added to the polymer for improving the mechanical properties of the polymer and reducing the amount of an expensive elastomer used in the printing element.

[0004]

Unexamined Japanese Patent Application Laid-Open Specification No. 2001-121833 (corresponding to EP 1080883 A) describes the use of a mixture of a silicone rubber and carbon black for producing a printing element, wherein the carbon black is used as a laser beam absorber. However, a photosensitive resin is not used in this invention. Unexamined Japanese Patent Application Laid-Open Specification No. 2001-328365 discloses the use of a graft-copolymer, wherein a non-porous silica having a particle diameter which is smaller than the wavelength of the visible light is added to the graft copolymer for improving the mechanical properties thereof. However, a photosensitive resin is not used in this invention and this patent document has no description about the use of a porous silica.

Unexamined Japanese Patent Application Laid-Open Specification No. 2002-3665 describes that silica may be added to a non-photosensitive resin as a reinforcing agent. That is,

the use of silica in this patent document does not extend beyond the customary use as a reinforcing agent, and besides, in this patent document, only a non-porous microparticulate silica is used in the Working Examples. Further, the resin used in this patent document is not a photosensitive resin and the resin is cured by heating. Therefore, the curing rate of the resin is low and the dimensional precision of a sheet obtained from the resin is poor.

[0005]

Each of Japanese Patent Nos. 2846954 and 2846955 (corresponding to U.S. Patent Nos. 5,798,202 and 5,804,353, respectively) discloses the use of a reinforced elastomer material obtained by mechanically, photochemically and thermochemically reinforcing a thermoplastic elastomer, such as SBS, SIS and SEBS. When a printing element formed from a thermoplastic elastomer is engraved with a laser beam having an oscillation wavelength within the infrared region, even portions of the printing element which are distant from the portion irradiated with the laser beam also tend to melt by heat. Therefore, the resultant printing element cannot be used for preparing an engraved pattern having a high resolution. For removing this problem, it is necessary to add a filler to the thermoplastic elastomer to thereby improve the mechanical properties thereof. In each of the above-mentioned patent documents, for improving the mechanical properties of the

thermoplastic elastomer and increasing the absorption of the laser beam by the thermoplastic elastomer, a large amount of carbon black having excellent ability to enhance the mechanical properties of a resin is added to a thermoplastic elastomer. However, since a large amount of carbon black is added to the elastomer, light transmittance of the elastomer is inevitably lowered, which is disadvantageous when it is attempted to perform a photochemical reinforcement of the elastomer. Therefore, when the above-mentioned reinforced elastomer material is subjected to laser engraving, it results in the generation of a large amount of debris (including viscous liquid material) which is difficult to remove. The generation of such debris not only necessitates a time-consuming treatment for removing the debris, but also causes problems, such as the occurrence of "edges" (i.e., edges formed by swollen resin) in the obtained relief pattern and the destruction of portions of the relief pattern which correspond to the dots of a print obtained using the relief pattern.

[0006]

Further, when a large amount of liquid debris, which is presumed to be a laser decomposition product of the resin, is generated during the laser engraving of the printing element, the liquid debris stains the optical parts of a laser engraving apparatus. When the liquid debris is adhered to the sur-

face of optical parts, such as a lens and a mirror, the resin causes serious troubles of the apparatus, such as burnout of the apparatus.

[0007]

[Problems to Be Solved by the Invention]

The object of the present invention is to provide a resin composition for forming a printing element which not only generates only a small amount of debris during the formation of a relief pattern directly on a printing element by laser engraving and enables an easy removal of the generated debris, but also is advantageous in that a precise image can be formed on the printing element by laser engraving and the resultant image-bearing printing plate has small surface tack.

[0008]

[Means to Solve the Problems]

In this situation, the present inventors have made extensive and intensive studies and found that the above-mentioned problems can be solved by using a specific photosensitive resin composition for forming a laser engravable printing element, wherein the photosensitive resin composition comprises (a) a resin which is in a solid state at 20 °C, (b) an organic compound having a polymerizable unsaturated group, and (c) an inorganic porous material having a specific surface area of from 10 m²/g to 1,500 m²/g, an average pore diameter of from 1 nm to 1,000 nm, a pore volume of from

0.1 ml/g to 10 ml/g and an oil absorption value of from 10 ml/100 g to 2,000 ml/100 g. Based on this novel finding, the present invention has been completed.

[0009]

Specifically, the present invention has been developed based on the idea of using in combination a resin which is easily molten or decomposed by laser beam irradiation and an inorganic porous material (c) for the absorption removal of the viscous liquid debris which is formed in a large amount by the melting or decomposition of the resin. In the present invention, inorganic microparticles are used as inorganic porous material (c) because they are not molten or deformed by laser beam irradiation and maintain their porous structure.

[0010]

That is, the present invention is concerned with:

1. A photosensitive resin composition for forming a laser engravable printing element, comprising:

- (a) a resin which is in a solid state at 20 °C,
- (b) an organic compound having a polymerizable unsaturated group, and
- (c) an inorganic porous material having a specific surface area of from 10 m²/g to 1,500 m²/g, an average pore diameter of from 1 nm to 1,000 nm, a pore volume of from 0.1 ml/g to 10 ml/g and an oil absorption value of from 10 ml/100 g to 2,000 ml/100 g.

2. The photosensitive resin composition according to item 1 above, wherein the resin (a) which is in a solid state at 20 °C has a number average molecular weight of from 5,000 to 300,000 and the organic compound (b) having a polymerizable unsaturated group has a number average molecular weight of less than 5,000.

3. The photosensitive resin composition according to item 1 above, wherein at least 30 % by weight of the resin (a), which is in a solid state at 20 °C, is at least one resin selected from the group consisting of a thermoplastic resin having a softening temperature of 500 °C or less and a solvent-soluble resin.

[0011]

4. The photosensitive resin composition according to item 1 above, wherein at least 20 % by weight of the organic compound (b) is a derivative of at least one compound selected from the group consisting of an alicyclic compound and an aromatic compound.

5. The photosensitive resin composition according to item 1 above, wherein the inorganic porous material (c) has a number average particle diameter of from 0.1 μm to 100 μm .

6. A laser engravable printing element produced by a process comprising:

shaping the photosensitive resin composition of any one of items 1 to 5 above into a sheet or cylinder, and

crosslink-curing the photosensitive resin composition by light or electron beam irradiation.

7. A multi-layered, laser engravable printing element comprising a printing element layer and at least one elastomer layer provided below the printing element layer, wherein the printing element layer is made of the laser engravable printing element of item 6 above and the elastomer layer has a Shore A hardness of from 20 to 70 and has a uniform thickness.

8. The multi-layered, laser engravable printing element according to item 7 above, wherein the elastomer layer is formed by curing a photosensitive resin composition which is in a liquid state at room temperature.

[0012]

[Mode for Carrying Out the Invention]

Hereinbelow, the present invention is explained in more detail, focusing on the preferred mode for carrying out the present invention. As resin (a) used in the present invention, both an elastomeric resin and a non-elastomeric resin can be used. It is preferred that at least 30 % by weight, more advantageously at least 50 % by weight, still more advantageously at least 70 % by weight of resin (a) used in the present invention is a thermoplastic resin. When at least 30 % by weight of resin (a) is a thermoplastic resin, a cured form of the photosensitive resin composition obtained using such resin (a) is satisfactorily fluidized when it is sub-

jected to laser beam irradiation and, therefore, the resultant fluidized resin composition is efficiently absorbed by inorganic porous material (c) contained in the resin composition. However, when the softening temperature of a thermoplastic resin used as resin (a) exceeds 350 °C, the shaping of the photosensitive resin composition into a sheet or cylinder must be performed at high temperatures. When the shaping is performed at high temperatures, there is a danger of denaturation and decomposition of organic compounds other than resin (a) contained in the photosensitive resin composition. Therefore, when a thermoplastic resin having a softening temperature above 350 °C is used, such a thermoplastic resin may be dissolved in a solvent and shaped by coating method.

[0013]

The technical characteristic of the present invention resides in the use of an inorganic porous material for the absorption removal of the liquid debris formed by laser beam irradiation. Therefore, it is preferred that resin (a) used in the present invention is a resin which is easily liquefied or decomposed by laser beam irradiation. Preferred examples of resins which are easily decomposed by laser beam irradiation include resins containing in the molecular chain thereof easily decomposable monomer units, such as monomer units derived from styrene, acrylates, methacrylates, ester compounds,

ether compounds, nitro compounds and alicyclic compounds. As representative examples of such easily decomposable resins, there can be mentioned polyethers, such as polyethylene glycol, polypropylene glycol and polytetraethylene glycol; aliphatic polycarbonates; and other resins, such as poly(methyl methacrylate), polystyrene, nitrocellulose, polyoxyethylene, polynorbornene, hydrated polycyclohexadiene and resins (such as a dendrimer) having many branched structures. As an index for evaluating the decomposability of a resin, there can be mentioned a weight loss which is measured under air by thermogravimetric analysis. The weight loss of resin (a) used in the present invention is preferably 50 % by weight or more at 500 °C. When the weight loss of a resin is 50 % by weight or more at 500 °C, such a resin can be satisfactorily decomposed by laser beam irradiation.

[0014]

There is no particular limitation with respect to the thermoplastic elastomers used in the present invention. As such thermoplastic elastomers, there can be mentioned styrene thermoplastic elastomers, such as SBS (polystyrene-polybutadiene-polystyrene), SIS (polystyrene-polyisoprene-polystyrene) and SEBS (polystyrene-polyethylene/polybutylene-polystyrene); olefin thermoplastic elastomers; urethane thermoplastic elastomers; ester thermoplastic elastomers; amide thermoplastic elastomers; and silicone thermoplastic

elastomers. A thermoplastic elastomer can be fluidized by heating and, thus, the fluidized thermoplastic elastomer can be easily mixed with inorganic porous material (c) which is an essential component of the present invention. In the present invention, the term "thermoplastic elastomer" means a polymer which has the ability to easily flow by heating and be easily processed into various shapes as in the case of other thermoplastic resins, and which shows rubber elasticity at room temperature. A thermoplastic elastomer contains a soft segment and a hard segment in the molecular structure thereof. The soft segment is formed by a polyether, a rubbery polymer or the like, and the hard segment is formed by a material which does not undergo plastic deformation at around room temperature as in the case of a vulcanized rubber. There are various types of hard segments, such as a frozen hard segment, a crystalline hard segment, a hydrogen bond hard segment and an ionically crosslinked hard segment.

[0015]

A suitable type of thermoplastic elastomer may be selected depending on the use of the ultimate printing plate. For example, when it is intended to use the printing plate produced using the photosensitive resin composition of the present invention in the field where the printing plate is required to exhibit a solvent resistance, it is preferred that the thermoplastic elastomer used for producing the pho-

tosensitive resin composition is a thermoplastic urethane elastomer, a thermoplastic ester elastomer, a thermoplastic amide elastomer or a thermoplastic fluoro elastomer, and when it is intended to use the printing plate in the field where the printing plate is required to have a heat resistance, it is preferred that the thermoplastic elastomer used for producing the photosensitive resin composition is a thermoplastic urethane elastomer, a thermoplastic olefin elastomer, a thermoplastic ester elastomer or a thermoplastic fluoro elastomer. Further, the strength of a cured form of the photosensitive resin composition can be varied greatly by changing the type of the thermoplastic elastomer used. When it is intended to use the photosensitive resin composition for producing a general purpose printing plate, it is preferred that the thermoplastic resin has a Shore A hardness in the range of from 20 to 75. On the other hand, when it is intended to use the photosensitive resin composition for producing a printing plate used for embossing (that is, for forming concavo-convex pattern on the surface of a paper, a film, a construction material or the like), a cured form of the resin composition is required to have relatively high hardness and, hence, it is preferred that the thermoplastic resin has a Shore D hardness in the range of from 30 to 80.

[0016]

There is no particular limitation with respect to the

non-elastomeric thermoplastic resin used in the present invention. For example, there can be mentioned a polyester resin, an unsaturated polyester resin, a polyamide resin, a polyamideimide resin, a polyurethane resin, an unsaturated polyurethane resin, a polysulfone resin, a polyethersulfone resin, a polyimide resin, a polycarbonate resin and a wholly aromatic polyester resin.

The softening temperature of the thermoplastic resin used in the present invention is preferably in the range of from 50 °C to 500 °C, more preferably from 80 °C to 350 °C, most preferably from 100 °C to 250 °C. When a photosensitive resin composition is produced using a thermoplastic resin having a softening temperature of 50 °C or more, such a photosensitive resin composition is in a solid state at room temperature and, thus, a shaped article obtained by shaping the photosensitive resin composition into a sheet or cylinder can be handled without suffering distortion of the shaped article. On the other hand, when a photosensitive resin composition is produced using a thermoplastic resin having a softening temperature of 500 °C or less, such a photosensitive resin composition can be shaped into a sheet or cylinder without employing a very high temperature and, therefore, there is no danger of denaturation or decomposition of other compounds contained in the photosensitive resin composition. In the present invention, the softening temperature of a

resin is a value determined by a dynamic viscoelastometer, and the softening temperature is defined as a temperature at which the viscosity of a resin changes drastically (in other words, a temperature at which the slope of the viscosity curve changes) when the temperature of the resin is elevated gradually from room temperature.

[0017]

Further, in the present invention, a solvent-soluble resin may also be used as resin (a). Specific examples of solvent-soluble resins include a polysulfone resin, a polyimide resin, a polyethersulfone resin, an epoxy resin, a bis-maleimide resin, a novolac resin, an alkyd resin, a polyolefin resin and a polyester resin.

[0018]

In general, most of the resins used as resin (a) in the present invention do not have a highly reactive, polymerizable unsaturated group in the molecular chain thereof. However, the resin used as resin (a) may have a highly reactive, polymerizable unsaturated group at a terminal(s) of a main chain thereof or in a side chain(s) thereof. When resin (a) having a highly reactive, polymerizable unsaturated group is used for producing a photosensitive resin composition, a printing element produced from such a photosensitive resin composition exhibits very high mechanical strength. However, when resin (a) has a highly reactive, polymerizable unsatu-

rated group in an amount such that the average number of the highly reactive, polymerizable unsaturated group per molecule is more than 2, the photosensitive resin composition suffers a marked cure shrinkage at the time of photocuring. Therefore, it is preferred that the average number of the highly reactive, polymerizable unsaturated group per molecule of resin (a) is 2 or less. The introduction of a polymerizable unsaturated group into a resin molecule is relatively easy, especially in the case of a thermoplastic polyurethane elastomer or a thermoplastic polyester elastomer. The "introduction of a highly reactive, polymerizable unsaturated group into a resin molecule" means that an unsaturated group is bonded to the terminal of a main chain or side chain of a resin, or to the non-terminal portion of a main chain or side chain of a resin. With respect to the method for obtaining a resin having a highly reactive, polymerizable unsaturated group, for example, there can be mentioned a method in which a polymerizable unsaturated group is directly introduced into the terminal of a polymer. As another example of the method for obtaining such a resin, there can be mentioned the following method. A reactive polymer is produced by introducing a plurality of reactive groups (such as a hydroxyl group, an amino group, an epoxy group, a carboxyl group, an acid anhydride group, a ketone group, a hydrazine group, an isocyanate group, an isothiocyanate group, a cyclic carbonate group and

an ester group) into a polymer as exemplified above, which has a molecular weight of several thousands. The produced reactive polymer is reacted with a binder compound having a plurality of binder groups capable of binding to the reactive groups of the polymer (for example, when the reactive groups of the polymer are hydroxyl groups or amino groups, a polyisocyanate can be used as the binder compound), to thereby adjust the molecular weight of the polymer and convert the terminals of the polymer into binder groups. Subsequently, an organic compound having a polymerizable unsaturated group as well as a group which is capable of reacting with the terminal binder groups of the reactive polymer is reacted with the reactive polymer to introduce the polymerizable unsaturated group into the terminals of the reactive polymer, thereby obtaining a resin having a highly reactive, polymerizable unsaturated group.

[0019]

The number average molecular weight of resin (a) is preferably in the range of from 5,000 to 300,000, more preferably from 7,000 to 200,000, still more preferably from 10,000 to 100,000. When a resin composition is produced using resin (a) having a number average molecular weight of 5,000 or more, the mechanical strength of the printing element produced from such a resin composition becomes satisfactory. On the other hand, when a resin composition is pro-

duced using resin (a) having a number average molecular weight of 300,000 or less, the removal of the debris formed by laser beam irradiation, namely a molten or decomposed resin, becomes satisfactory. In the present invention, the number average molecular weight is determined by gel permeation chromatography (GPC) in which a calibration curve prepared using standard polystyrene samples having a known molecular weight is employed.

[0020]

Organic compound (b) used for producing the photosensitive resin composition of the present invention is a compound having an unsaturated bond which participates in a radical polymerization reaction or an addition polymerization reaction. From the viewpoint of ease in blending organic compound (b) with resin (a), the number average molecular weight of the organic compound (b) is preferably less than 5,000. Specific examples of organic compound (b) include olefins, such as ethylene, propylene, styrene and divinylbenzene; acetylene type compounds; (meth)acrylic acid and derivatives thereof; haloolefins; unsaturated nitriles, such as acrylonitrile; (meth)acrylamide and derivatives thereof; allyl compounds, such as allyl alcohol and allyl isocyanate; unsaturated dicarboxylic acids (such as maleic anhydride, maleic acid and fumaric acid) and derivatives thereof; vinyl acetate; N-vinylpyrrolidone; N-vinylcarbazole and cyanates.

From the viewpoint of various advantages of products, such as availability and reasonable price, (meth)acrylic acid and derivatives thereof are preferred.

[0021]

Examples of derivatives of the compounds mentioned above as compound (b) include compounds having an alicyclic group, such as a cycloalkyl group, a bicycloalkyl group, a cycloalkene group or a bicycloalkene group; compounds having an aromatic group, such as a benzyl group, a phenyl group or a phenoxy group; compounds having a group, such as an alkyl group, a halogenated alkyl group, an alkoxyalkyl group, a hydroxyalkyl group, an aminoalkyl group, a tetrahydrofurfuryl group, an allyl group or a glycidyl group; and esters with a polyol, such as an alkylene glycol, a polyoxyalkylene glycol, an (alkyl/allyloxy)polyalkylene glycol or trimethylol propane.

[0022]

The above-mentioned compounds (b) having a polymerizable unsaturated group can be used individually or in combination depending on the use of the photosensitive resin composition. For example, when the printing element formed from the photosensitive resin composition of the present invention is used for producing a printing plate, for suppressing the swelling of the printing plate by a solvent used in a printing ink (i.e., an organic solvent, such as an alcohol or an ester), it is preferred that the organic compound (b) used for pro-

ducing the photosensitive resin composition is at least one derivative of a compound selected from the group consisting of a long chain aliphatic compound, an alicyclic compound and an aromatic compound.

In the present invention, for improving the mechanical strength of a printing element obtained from the photosensitive resin composition of the present invention, it is preferred that at least 20 % by weight, more advantageously at least 50 % by weight of organic compound (b) is a derivative of at least one compound selected from the group consisting of an alicyclic compound and an aromatic compound.

For improving the impact resilience of a printing plate obtained from the photosensitive resin composition of the present invention, the type of the organic compound (b) may be appropriately selected, based on the conventional knowledge on photosensitive resin compositions for forming printing plates (for example, a methacrylic monomer described in Unexamined Japanese Patent Application Laid-Open Specification No. Hei 7-239548 can be used).

[0023]

Inorganic porous material (c), which is an essential component of the photosensitive resin composition of the present invention, is inorganic microparticles having micropores and/or very small voids. In the present invention, inorganic porous material (c) is used to perform an absorption removal

of viscous liquid debris which is generated in a large amount during the laser engraving of a printing plate formed from the photosensitive resin composition of the present invention. Further, the presence of inorganic porous material (c) prevents the occurrence of surface tack of the printing plate. In the present invention, the main purpose of the use of inorganic porous material (c) is the removal of a viscous liquid debris, and the characteristics and properties of inorganic porous material (c), such as a number average particle diameter, a specific surface area, an average pore diameter, a pore volume and an ignition loss, are very important factors for achieving an efficient removal of the viscous liquid debris.

[0024]

In the present invention, a resin which can be easily decomposed by laser beam irradiation is used to produce the photosensitive resin composition of the present invention and, hence, when linkages in the polymer chains of the resin are broken by laser beam, viscous liquid debris composed of low molecular weight components (i.e., monomers and oligomers) is generated in a large amount. In the present invention, inorganic porous material (c) is used to perform an absorption removal of the generated viscous liquid debris. The removal of viscous liquid debris by the inorganic porous material is a completely novel technique which has not conventionally

been known and the use of such a novel technique is the major characteristic feature of the present invention. Therefore, as mentioned above, the characteristics and properties of inorganic porous material (c) (e.g., porous silica), such as a number average particle diameter, a specific surface area, an average pore diameter, a pore volume, an ignition loss and an oil absorption value, are very important factors for achieving an efficient removal of a viscous liquid debris. For example, when porous material (c) is selected from the conventional porous silica, it should be noted that porous silica, such as fumed silica, contains non-porous microparticles and porous microparticles having too small pores to absorb the liquid debris satisfactorily, and such microparticles alone exhibit only poor ability to remove the viscous liquid debris. In addition, the molecular weight and viscosity of the resin also have a great influence on the efficiency of the removal of the viscous liquid debris.

[0025]

In the present invention, it is preferred that the number average particle diameter of the inorganic porous material (c) is in the range of from 0.1 μm to 100 μm . When a porous material having a number average particle diameter of less than 0.1 μm is used in the photosensitive resin composition, disadvantages are likely to be caused wherein a dust arises during the laser engraving of the printing element

formed from the photosensitive resin composition, thereby causing the engraving apparatus to be contaminated with dust. Further, when such an inorganic porous material is mixed with resin (a) and organic compound (b), the resultant mixture is likely to pose problems, such as an increase in the viscosity of the resultant mixture, an incorporation of air bubbles into the mixture, and a generation of dust. On the other hand, when an inorganic porous material having a number average particle diameter of more than 100 μm is used to produce a photosensitive resin composition, disadvantages are likely to be caused wherein a relief pattern formed on a printing plate by laser engraving is chipped, so that an image of a print obtained using the relief pattern becomes imprecise. The number average particle diameter of the inorganic porous material (c) is more preferably in the range of from 0.5 μm to 20 μm , still more preferably in the range of from 3 μm to 10 μm . In the present invention, the average particle diameter of the inorganic porous material is determined by using a laser scattering particle size distribution analyzer "LA910" (trade name; manufactured and sold by Horiba Ltd.).

[0026]

The specific surface area of inorganic porous material (c) is in the range of from 10 m^2/g to 1,500 m^2/g , preferably from 100 m^2/g to 800 m^2/g . When the specific surface area of an inorganic porous material is 10 m^2/g or more, the ability

thereof to remove the liquid debris generated during laser engraving becomes satisfactory. On the other hand, when the specific surface area of an inorganic porous material is not more than $1,500 \text{ m}^2/\text{g}$, it becomes possible to suppress the increase in the viscosity of the photosensitive resin composition and also suppress the thixotropy of the photosensitive resin composition. In the present invention, the specific surface area is determined by the BET method using the nitrogen adsorption isotherm obtained at -196°C .

[0027]

The average pore diameter of inorganic porous material (c) has a great influence on the ability thereof to absorb the liquid debris which is generated during the laser engraving. The average pore diameter is preferably in the range of from 1 nm to 1,000 nm, more preferably from 2 nm to 200 nm, still more preferably from 2 nm to 50 nm. When the average pore diameter of an inorganic porous material is 1 nm or more, such an inorganic porous material is capable of absorbing a satisfactory amount of the liquid debris generated during the laser engraving. On the other hand, when the average pore diameter of an inorganic porous material is not more than 1,000 nm, the specific surface area of such an inorganic porous material becomes large enough to absorb a satisfactory amount of the liquid debris. The reason why an inorganic porous material having an average pore diameter of less than

1 nm cannot absorb a satisfactory amount of the liquid debris is not fully elucidated, but it is considered that the viscous liquid debris is difficult to enter into the micropores having such a small average pore diameter and hence, only a small amount of the liquid debris is absorbed by such particles. For example, a zeolite, a mordenite, a hollandite, a todorokite and a faujasite are porous materials having micropores of less than 1 nm. Each of these porous materials has a large specific surface area; however, their ability to remove the liquid debris is low. In the present invention, the average pore diameter is determined by the nitrogen adsorption method. Among various porous materials, those which have an average pore diameter of from 2 to 50 nm are called "mesoporous materials". Such mesoporous materials are especially preferred in the present invention because the mesoporous materials have remarkably high ability to absorb the liquid debris. In the present invention, the pore diameter distribution is determined from a nitrogen adsorption isotherm obtained at -196°C .

[0028]

The pore volume of inorganic porous material (c) is in the range of from 0.1 ml/g to 10 ml/g, preferably from 0.2 ml/g to 5 ml/g. When the pore volume of an inorganic porous material is 0.1 ml/g or more, such an inorganic porous material is capable of absorbing a satisfactory amount of the

viscous liquid debris generated during the laser engraving. On the other hand, when the pore volume is not more than 10 ml/g, the inorganic porous material is capable of maintaining its mechanical properties. In the present invention, the pore volume is a value determined by the nitrogen adsorption method. Specifically, the pore volume is determined from a nitrogen adsorption isotherm obtained at -196 °C.

[0029]

The oil absorption value is an index for evaluating the amount of a liquid debris which an inorganic porous material can absorb, and it is defined as an amount of an oil absorbed by 100 g of the inorganic porous material. The oil absorption value of the inorganic porous material (c) used in the present invention is preferably in the range of from 10 ml/100 g to 2,000 ml/100 g, more preferably from 50 ml/100 g to 1,000 ml/100 g. When the oil absorption value of an inorganic porous material is 10 ml/100 g or more, such an inorganic porous material can effectively remove the liquid debris generated by laser engraving. On the other hand, when the oil absorption value of an inorganic porous material is not more than 2,000 ml/100 g, such an inorganic porous material can maintain satisfactory level of the mechanical properties. The oil absorption value is determined in accordance with JIS-K5101.

[0030]

It is preferred that inorganic porous material (c) used in the present invention maintains its porous structure without suffering distortion or melting by laser beam irradiation, especially infrared radiation. Therefore, it is desired that the ignition loss of inorganic porous material (c) at 950 °C for 2 hours is not more than 15 % by weight, preferably not more than 10 % by weight.

There is no particular limitation with respect to the shape of the particles of inorganic porous material (c), and each particle of inorganic porous material (c) may independently be in the form of a sphere, a plate or a needle. Alternatively, inorganic porous material (c) may not have any definite shape or may be in the form of particles each having a projection(s) on the surface thereof. Further, inorganic porous material (c) may be in the form of hollow particles or spherical granules, such as silica sponge, which have uniform pore diameter. Specific examples of inorganic porous material (c) include a porous silica, a mesoporous silica, a silica-zirconia porous gel, a porous alumina and a porous glass. In addition, a lamellar substance, such as a lamellar clay compound, having voids between the layers can be also used as inorganic porous material (c), wherein the dimension of each void (distance between the layers) ranges from several to 100 nm. Since a pore diameter cannot be defined for such a lamellar substance, the dimension of the void between the lay-

ers thereof (i.e., the distance between the layers) is defined as a pore diameter.

[0031]

In the present invention, inorganic porous material (c) having incorporated in its pores and/or voids an organic colorant (such as a pigment or a dye) which is capable of absorbing light having a wavelength of a laser beam can be used.

Further, the surface of the inorganic porous material may be modified by coating the surface thereof with a silane coupling agent, a titanium coupling agent or an organic compound, to thereby obtain particles having an improved hydrophilic or hydrophobic property.

In the present invention, the substances exemplified above as inorganic porous material (c) can be used individually or in combination. By the addition of inorganic porous material (c) to the photosensitive resin composition, it becomes possible to suppress the generation of liquid debris during the laser engraving of the printing element, and the resultant image-bearing printing plate has small surface tack.

[0032]

The amounts of resin (a), organic compound (b) and inorganic porous material (c) which are used in the photosensitive resin composition of the present invention are as follows. In general, the amount of organic compound (b) is preferably 5 to 200 parts by weight, more preferably 20 to

100 parts by weight, relative to 100 parts by weight of resin (a). The amount of inorganic porous material (c) is preferably 1 to 100 parts by weight, more preferably 2 to 50 parts by weight, still more preferably 2 to 20 parts by weight, relative to 100 parts by weight of resin (a).

When the amount of organic compound (b) is less than 5 parts by weight, a printing plate or the like which is obtained from the photosensitive resin composition is likely to suffer from disadvantages, such as a difficulty in maintaining a good balance between the rigidity of the composition, and the tensile strength and elongation of the composition. When the amount of organic compound (b) exceeds 200 parts by weight, the photosensitive resin composition is likely to suffer from not only a marked cure shrinkage at the time of the crosslink-curing of the resin composition, but also a lowering of the uniformity in thickness of the resultant printing element.

[0033]

When the amount of inorganic porous material (c) is less than 1 part by weight, depending on the types of resin (a) and organic compound (b) used, the prevention of surface tack and the removal of the liquid debris generated by laser engraving become unsatisfactory. On the other hand, when the amount of inorganic porous material (c) exceeds 100 parts by weight, a printing plate which is obtained using the photo-

sensitive resin composition becomes fragile and loses transparency. Especially when a flexographic printing plate is produced using a resin composition containing too large an amount of inorganic porous material (c), the rigidity of such a flexographic printing plate may become too high. When a laser engravable printing element is formed by photocuring a photosensitive resin composition (especially when the photocuring is performed using UV light), the light transmittance of the resin composition influences the curing reaction. Therefore, as inorganic porous material (c), it is advantageous to use an inorganic porous material having a refractive index which is close to that of the photosensitive resin composition.

[0034]

Specific examples of methods for mixing the inorganic porous material (c) with other components include a method in which a thermoplastic resin is fluidized by heating to thereby obtain a molten resin (a), and inorganic porous material (c) is directly added to the molten resin (a); and a method in which a thermoplastic resin and photopolymerizable organic compound (b) are kneaded, and inorganic porous material (c) is added thereto. It is preferred, however, to avoid the use of a method in which inorganic porous material (c) is directly added to photopolymerizable organic compound (b) having such a low molecular weight prior to the mixing

with resin (a), since the use of such method may reduce the ability of inorganic porous material (c) to absorb the liquid debris generated during laser engraving. The reason for such phenomenon is not fully elucidated, but it is considered that, in the photosensitive resin composition produced by employing such method, the organic compound (b) having low viscosity enters into the micropores or voids of each particle of inorganic porous material (c) and, hence, when the photosensitive resin composition is subjected to an exposure process in the production of a printing element, the photopolymerizable organic compound (b) enclosed in the micropores or voids of inorganic porous material (c) is cured, thus filling up the micropores or voids of inorganic porous material (c).

[0035]

In the production of a laser engravable printing element from the photosensitive resin composition of the present invention, the photosensitive resin composition is crosslink-cured by irradiation thereof with a light or an electron beam so as to impart the properties of a printing element to the photosensitive resin composition. The photosensitive resin composition may further comprise a polymerization initiator. A polymerization initiator can be appropriately selected from those which are customarily used. Examples of polymerization initiators usable in the present invention include a radical polymerization initiator, a cationic poly-

merization initiator and an anionic polymerization initiator, which are exemplified in "Koubunshi Deta Handobukku - Kisohe (Polymer Data Handbook - Fundamentals)" edited by Polymer Society, published in 1986 by Baifukan Co., Ltd. In the present invention, the crosslink-curing of the photosensitive resin composition which is performed by photopolymerization using a photopolymerization initiator is advantageous for improving the productivity of the printing element while maintaining the storage stability of the resin composition. The crosslink-curing of the photosensitive resin composition of the present invention may be performed by using conventional photopolymerization initiators. Representative examples of conventional photopolymerization initiators which can be used in the present invention include benzoin; benzoin alkyl ethers, such as benzoin ethyl ether; acetophenones, such as 2-hydroxy-2-methylpropiophenone, 4'-isopropyl-2-hydroxy-2-methylpropiophenone, 2,2-dimethoxy-2-phenylacetophenone and diethoxyacetophenone; photoradical polymerization initiators, such as 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propane-1-one, methyl phenylglyoxylate, benzophenone, benzil, diacetyl, diphenylsulfide, eosin, thionine and anthraquinone; photocationic polymerization initiators, such as aromatic diazonium salt, an aromatic iodonium salt and an aromatic sulfonium salt, each of which generates an acid by absorbing a light; and

polymerization initiators, each of which generates a base by absorbing a light. The polymerization initiator is preferably used in an amount of from 0.01 to 10 % by weight, based on the total weight of resin (a) and organic compound (b).

[0036]

In addition, depending on the use and desired properties of the photosensitive resin composition, other additives, such as a polymerization inhibitor, an ultraviolet absorber, a dye, a pigment, a lubricant, a surfactant, a plasticizer and a fragrance, may be added to the photosensitive resin composition.

With respect to the method for shaping the photosensitive resin composition of the present invention into a sheet or cylinder, any of conventional methods employed for shaping resins can be employed. For example, there can be mentioned an injection molding method; a method in which a resin is extruded from a nozzle or a die by using a pump or extruder, followed by adjustment of the thickness of the extruded resin using a blade; and a method in which a resin is subjected to calendar processing using a roll, thereby obtaining a resin sheet having a desired thickness. During the shaping of the resin composition, the resin composition can be heated at a temperature which does not cause the lowering of the properties of the resin.

[0037]

Further, if desired, the shaped resin composition may be subjected to a treatment using a pressure roll or an abrasion treatment. In general, the resin composition is shaped on an underlay called "back film" which is made of PET, nickel or the like. Alternatively, the resin composition can be shaped directly on a cylinder of a printing machine. The function of the above-mentioned "back film" is to impart dimensional stability to the printing element. Therefore, it is preferred to use a back film having a high dimensional stability. Preferred materials for the back film are materials having a coefficient of linear thermal expansion of not more than 100 ppm/°C, more advantageously not more than 70 ppm/°C. Specific examples of materials for the back film include a polyester resin, a polyimide resin, a polyamide resin, a polyamideimide resin, a polyetherimide resin, a poly-bis-maleimide resin, a polysulfone resin, a polycarbonate resin, a polyphenylene ether resin, a polyphenylene thioether resin, a polyethersulfone resin, a liquid crystal resin composed of a wholly aromatic polyester resin, a wholly aromatic polyamide resin, and an epoxy resin. Of these resins, a plurality of different resins may be used to produce a back film which is a laminate of layers of different resins. For example, a sheet formed by laminating a 50 μm -thick polyethylene terephthalate sheet on each side of a 4.5 μm -thick wholly aromatic polyamide film can be used.

[0038]

As a method for decreasing the coefficient of linear thermal expansion of the back film, there can be mentioned a method in which a filler is added to the back film, and a method in which a meshed cloth of a wholly aromatic polyamide or the like, a glass cloth or the like is impregnated or coated with a resin. The fillers added to the back film may be conventional fillers, such as organic microparticles, inorganic microparticles of metal oxides or metals, and organic-inorganic composite microparticles. Further, the fillers may be porous microparticles, hollow microparticles, encapsulated microparticles or particles of compounds having a lamellar structure in which a low molecular weight compound is intercalated. Especially useful are microparticles of metal oxides, such as alumina, silica, titanium oxide and zeolite; latex microparticles comprised of a polystyrene-polybutadiene copolymer; and natural organic microparticles, such as a highly crystalline cellulose.

[0039]

The back film used in the present invention may be subjected to physical treatment or chemical treatment so as to improve the adhesion of the back film to the photosensitive resin composition layer or an adhesive agent layer formed on the back film. With respect to the physical treatment, there can be mentioned a sand blast method, a wet blast method (in

which a liquid suspension of microparticles is sprayed), a corona discharge treatment, a plasma treatment, a UV light irradiation and a vacuum UV light irradiation. With respect to the chemical treatment, there can be mentioned a treatment with a strong acid, a strong alkali, an oxidation agent or a coupling agent.

[0040]

The thus obtained shaped photosensitive resin composition is crosslink-cured by light or electron beam irradiation to obtain a printing element. The photosensitive resin composition may also be crosslink-cured by light or electron beam irradiation while shaping the photosensitive resin composition. However, it is preferred to perform the crosslink-curing with light since a simple apparatus can be used, and a printing element having a uniform thickness can be obtained. With respect to the light source used for curing, there can be mentioned a high pressure mercury lamp, an ultra-high pressure mercury lamp, an ultraviolet fluorescent lamp, a carbon arc lamp and a xenon lamp. The curing of the resin composition can be also performed by any other conventional methods for curing a resin composition. The photocuring can be performed by irradiating a light from a single light source, but lights of different light sources may be used in combination because the rigidity of the cured resin composition can be improved by performing the photocuring by two or

more lights having different wavelengths.

[0041]

The thickness of the laser engravable printing element of the present invention can be appropriately selected depending on the use of the printing element. When the printing element is used for producing a printing plate, the thickness of the printing element is generally in the range of from 0.1 to 7 mm. Further, the printing element may be a multi-layered printing element comprising a plurality of layers made of different materials.

In the present invention, a cushion layer formed from an elastomer can be provided below the printing element layer, thereby forming a multi-layered, laser engravable printing element. In general, the depth of the laser engraving on the printing element layer is 0.1 mm to several millimeters. The portion of the printing element which is positioned below the engraved portion may be made of a material other than the photosensitive resin composition of the present invention. It is preferred that the elastomer layer which functions as a cushion layer has a Shore A hardness of from 20 to 70. When the Shore A hardness of the elastomer layer is 20 or more, the elastomer layer is capable of changing its shape appropriately so as to maintain the printing quality of the printing plate. When the Shore A hardness is not more than 70, such an elastomer layer is capable of functioning as a cush-

ion layer. The Shore A hardness of the elastomer layer is more preferably from 30 to 60.

[0042]

There is no particular limitation with respect to an elastomer used as a raw material for the cushion layer so long as the elastomer has rubber elasticity. As elastomers usable as raw materials for the elastomer layer, there can be mentioned a thermoplastic elastomer, a photocurable elastomer and a thermocurable elastomer. A porous elastomer having nanometer-size micropores can be also used. From the viewpoint of ease in producing a printing plate having a shape of a sheet or cylinder, it is preferred that the elastomer layer is produced by photocuring a resin which is in a liquid state (that is, a raw material which becomes an elastomer after being photocured).

[0043]

Specific examples of thermoplastic elastomers used for producing the cushion layer include styrene thermoplastic elastomers, such as SBS (polystyrene-polybutadiene-polystyrene), SIS (polystyrene-polyisoprene-polystyrene) and SEBS (polystyrene-polyethylene/polybutylene-polystyrene); olefin thermoplastic elastomers; urethane thermoplastic elastomers; ester thermoplastic elastomers; amide thermoplastic elastomers; silicone thermoplastic elastomers; and fluoro thermoplastic elastomers.

[0044]

As the photocurable elastomers, there can be mentioned a mixture obtained by mixing the above-mentioned thermoplastic elastomer with a photopolymerizable monomer, a plasticizer, a photopolymerization initiator and the like; and a liquid composition obtained by mixing a elastomer resin with a photopolymerizable monomer, a photopolymerization initiator and the like. In the present invention, differing from the production of a printing plate using a conventional printing element, in which a precise mask image should be formed on the printing element using light, the resin composition is cured by exposing the entire surface of the shaped article of the resin composition to light and, thus, it is not necessary to use a material having properties which are conventionally needed to form precise pattern on the printing element. Therefore, so long as the resin composition exhibits a satisfactory level of mechanical strength, there is a considerable freedom of choice with respect to the raw materials used for producing the resin composition.

[0045]

In addition to the elastomers mentioned above, it is also possible to use vulcanized rubbers, organic peroxides, primary condensates of a phenolic resin, quinone dioxime, metal oxides and non-vulcanized rubbers, such as thiourea.

Further, it is also possible to use an elastomer ob-

tained by three dimensionally crosslinking a telechelic liquid rubber by using a curing agent therefor.

In the production of a multi-layered printing element, a back film may be formed either below the cushion layer (that is, below the bottom of the printing element) or in between the photosensitive resin composition layer and the elastomer layer (that is, at a central portion of the multi-layered printing element).

In addition, a modifier layer may be provided on the surface of the laser engravable printing element of the present invention so as to decrease the surface tack and improve the ink wettability of the printing plate. Examples of modifier layers include a coating formed by a surface treatment with a compound, such as a silane coupling agent or a titanium coupling agent, which reacts with hydroxyl groups present on the surface of the printing element; and a polymer film containing porous inorganic particles.

[0046]

As a compound which is widely used as a silane coupling agent, there can be mentioned a compound having in the molecule thereof a functional group which is highly reactive with hydroxyl groups present on the surface of a substrate. Examples of such functional groups include a trimethoxysilyl group, a triethoxysilyl group, a trichlorosilyl group, a diethoxysilyl group, a dimethoxysilyl group, a dimonochloro-

silyl group, a monoethoxysilyl group, a monomethoxysilyl group and a monochlorosilyl group. At least one of these functional groups is present in each molecule of the silane coupling agent and the molecule is immobilized on the surface of a substrate by the reaction between the functional group and the hydroxyl groups present on the surface of the substrate. Further, the compound used as a silane coupling agent in the present invention may further contain in the molecule thereof at least one reactive functional group selected from the group consisting of an acryloyl group, a methacryloyl group, an amino group containing an active hydrogen, an epoxy group, a vinyl group, a perfluoroalkyl group and a mercapto group, and/or a long chain alkyl group.

[0047]

Examples of titanium coupling agents include isopropyltriisostearoyl titanate, isopropyltris(dioctylpyrophosphate) titanate, isopropyltri(N-aminoethyl-aminoethyl) titanate, tetraoctylbis(di-tridecylphosphite) titanate, tetra(2,2-diallyloxymethyl-1-butyl)bis(di-tridecyl)phosphite titanate, bis(octylpyrophosphate)oxyacetate titanate, bis(dioctylpyrophosphate)ethylene titanate, isopropyltrioctanoyl titanate, isopropylldimethacrylisostearoyl titanate, isopropyltridodecylbenzenesulfonyl titanate, isopropylisostearoyldiacryl titanate, isopropyltri(dioctylsulfate) titanate, isopropyltricumylphenyl titanate and tetraisopropylbis(dioctyl-

phosphite) titanate.

[0048]

When the coupling agent which is immobilized on the surface of the printing plate has a polymerizable reactive group, the immobilized coupling agent may be crosslinked by irradiation with light, heat or electron beam to thereby further improve the strength of a coating formed by the coupling agent.

If desired, the above-mentioned coupling agent may be diluted with a mixture of water and an alcohol or a mixture of an aqueous acetic acid and an alcohol, to thereby obtain a coupling agent solution. The concentration of the coupling agent in the solution is preferably 0.05 to 10.0 % by weight.

[0049]

Hereinbelow, explanations are made on the methods for performing a coupling agent treatment. The above-mentioned coupling agent solution is applied onto the surface of the printing element or the printing plate after laser engraving, to thereby form a coating of the coupling agent. There is no particular limitation with respect to the method for applying the coupling agent solution. For example, the application of the coupling agent solution may be performed by an immersing method, a spraying method, a roll coating method or a coating method using a brush. There is no particular limitation with respect to the coating temperature and the coating time, but it is preferred that the coating is performed at 5 to 60 °C

for 0.1 to 60 seconds. It is preferred that the drying of the coupling agent solution layer formed on the surface of the printing element or the printing plate is performed by heating, and the preferred heating temperature is 50 to 150 °C.

[0050]

Before treating the surface of the printing element or printing plate with a coupling agent, the surface of the printing element or printing plate may be irradiated with vacuum ultraviolet light having a wavelength of not more than 200 nm by a xenon excimer lamp or exposed to a high energy atmosphere (such as plasma), to thereby generate hydroxyl groups on the surface of the printing element or printing plate. The thus generated hydroxyl groups are used to immobilize the coupling agent on the surface of the printing element or printing plate, so that the coupling agent can be immobilized in a high density on the surface of the printing element or printing plate.

When a printing element layer containing the particulate inorganic porous material is exposed at the surface of a printing plate, such a printing plate may be treated under a high energy atmosphere, such as plasma, so as to etch the surface (formed of an organic substance) slightly, thus forming minute concavo-convex portions on the surface of the printing plate. This treatment may decrease the surface tack

and improve the ink wettability of the printing plate because the treatment enables the particulate inorganic porous material to absorb an ink more easily.

[0051]

In a laser engraving process, a desired image is converted into digital data, and a relief pattern (corresponding to the desired image) is formed on the printing element by controlling a laser irradiation apparatus by a computer having the above-mentioned digital data. The laser used for the laser engraving may be any type of lasers so long as the laser comprises a light having a wavelength which can be absorbed by the printing element. For performing the laser engraving quickly, it is preferred that the output of the laser is as high as possible. Specifically, infrared lasers or solid state lasers operating in the infrared region, such as a carbon dioxide laser, a YAG laser and a semiconductor laser, are preferred. Further, ultraviolet lasers having an oscillation in a ultraviolet light range, such as an excimer laser, a YAG laser tuned to the third or fourth harmonics and a copper vapor laser, may be used for an abrasion treatment (which breaks the linkages in the organic compounds) and hence, are suitable for forming precise patterns. The laser irradiation may be either a continuous irradiation or a pulse irradiation. In general, a resin absorbs a light having a wavelength around 10 μm and, therefore, when a carbon dioxide laser hav-

ing an oscillation wavelength around 10 μm is used, there is no need to add a component for facilitating the absorption of the laser beam. However, when a YAG laser which has an oscillation wavelength of 1.06 μm is used, since most organic compounds do not absorb light having a wavelength of 1.06 μm , it is preferred to add a component, such as a dye or a pigment, for facilitating the absorption of a laser beam. Examples of dyes include a poly(substituted)-phthalocyanine compound and a metal-containing phthalocyanine compound, a cyanine compound, a squalilium dye, a chalcogenopyryloallylidene dye, a chloronium dye, a metal thiolate dye, a bis(chalcogenopyrylo)polymethine dye, an oxyindolidene dye, a bis(aminoaryl)polymethine dye, a melocyanine dye and a quinoid dye. Examples of pigments include dark colored inorganic pigments, such as carbon black, graphite, copper chromite, chromium oxide, cobalt chromium aluminate and iron oxide; powders of metals, such as iron, aluminum, copper and zinc, and doped metal powders which are obtained by doping any of the above-mentioned metal powders with Si, Mg, P, Co, Ni, Y or the like. These dyes and pigments can be used individually or in combination. When a plurality of different dyes or pigments are used in combination, they can be combined in any form. For example, different dyes or pigments may be used together in such a form as having a laminate structure.

[0052]

The laser engraving is performed in an atmosphere of oxygen-containing gas, generally in the presence of or under the flow of air; however, it can be also performed in an atmosphere of carbon dioxide gas or nitrogen gas. After completion of the laser engraving, powdery or liquid debris which is present in a small amount on the surface of the resultant relief printing plate may be removed by an appropriate method, such as washing with a mixture of water with a solvent or surfactant, high pressure spraying of an aqueous detergent or spraying of a high pressure steam.

The printing element of the present invention can be advantageously used not only for forming a relief pattern of a printing plate, but also for the production of a stamp and seal; a design roll for embossing; a relief pattern for patterning a paste used for producing an electronic circuit, such as a resistive material and a conductive material; a relief pattern for a mold used for producing pottery; a relief pattern for an advertisement or display board; and molds for various molded articles.

[0053]

Hereinbelow, the present invention will be described in more detail with reference to the following Examples and Comparative Examples, but they should not be construed as limiting the scope of the present invention.

In the following Examples and Comparative Examples, laser engraving was performed by TYP STAMPLAS SN 09 (trade name) which is manufactured and sold by Baasel Lasertech. The laser engraved pattern included portions corresponding to halftone dots, 500 μ m-wide relief lines (convex lines) and 500 μ m-wide reverse lines (grooves). The laser engraving was performed under conditions wherein the engraving depth is 0.55 mm.

[0054]

Debris on the printing element after laser engraving was wiped away with a nonwoven fabric (trade name: BEMCOT M-3; manufactured and sold by Asahi Kasei Corporation) which was impregnated with ethanol or acetone. Further, the weight of a printing element before laser engraving, the weight of the printing element immediately after the laser engraving and the weight of a relief printing plate after wiping were measured. The relative amount of the residual debris was calculated in accordance with the following formula (1):

$$\frac{[(\text{Weight of a printing element immediately after laser engraving}) - (\text{Weight of a relief printing plate after wiping})]}{[(\text{Weight of a printing element before laser engraving}) - (\text{Weight of a relief printing plate after wiping})]} \times 100 \quad (1)$$

[0055]

Tack on the surface of a relief printing plate after wiping was measured by a tack tester (manufactured and sold by Toyo Seiki Seisaku-Sho Ltd.). Specifically, an aluminum ring having a radius of 50 mm and a width of 13 mm was attached to a smooth portion of a relief printing plate (test specimen) at 20 °C so that the aluminum ring stood vertically on the specimen. A load of 0.5 kg was applied to the aluminum ring for 4 seconds. Subsequently, the aluminum ring was pulled at a rate of 30 mm per minute and the resisting force at the time of the detachment of the aluminum ring was measured by a push-pull gauge. The larger the resisting force, the larger the surface tack (tackiness) of the specimen.

With respect to the laser engraved printing plate (having a relief pattern formed thereon), the portions of the relief pattern which correspond to the halftone dots (screen ruling = 80 lpi, and total area of halftone dots = approximately 10 %, based on the halftone area of a print obtained using the engraved pattern) were observed under an electron microscope.

[0056]

[Examples 1 to 4 and Comparative Examples 1 and 2]

A photosensitive resin composition was produced using a styrene-butadiene copolymer (hereinafter, referred to as "SBS") (trade name: Tufprene A; manufactured and sold by Asahi Kasei Corporation) as a thermoplastic elastomer resin

which is in a solid state at 20 °C (i.e., resin (a)) and other components (polymerizable monomer (i.e., organic compound (b)), inorganic porous materials (c), photopolymerization initiator and other additives) which are shown in Table 1. The inorganic porous materials used were the following porous microparticulate silica products manufactured and sold by Fuji Silysia Chemical Ltd.: "SYLOSPHERE C-1504" (trade name) (abbreviated to "C-1504") (number average particle diameter: 4.5 μm , specific surface area: 520 m^2/g , average pore diameter: 12 nm, pore volume: 1.5 ml/g, ignition loss: 2.5 % by weight and oil absorption value: 290 ml/100 g); "SYLOPHOBIC 4004" (trade name) (abbreviated to "CH-4004") (number average particle diameter: 8.0 μm , specific surface area: 300 m^2/g , average pore diameter: 17 nm, pore volume: 1.25 ml/g, ignition loss: 5.0 % by weight and oil absorption value: 200 ml/100 g); and "SYLYSIA 470" (trade name) (abbreviated to "C-470") (number average particle diameter: 14.1 μm , specific surface area: 300 m^2/g , average pore diameter: 17 nm, pore volume: 1.25 ml/g, ignition loss: 5.0 % by weight, oil absorption value: 180 ml/100 g). In addition, a zeolite (number average particle diameter: 2.9 μm , specific surface area: 18 m^2/g , average pore diameter: 0.9 nm and oil absorption value: 45 ml/100 g) was also used as an inorganic porous material. The obtained photosensitive resin composition was shaped into a sheet (thickness: 2.8 mm) on a PET film. Then,

the resultant sheet was photocured by ALF type 213E exposure apparatus (manufactured and sold by Asahi Kasei Corporation). The exposure was performed for 10 minutes in vacuo, in which the upper surface of the sheet (on which a relief pattern was to be formed) was exposed at 2000 mJ/cm^2 and the other surface of the sheet was exposed at 1000 mJ/cm^2 , thereby obtaining a printing element.

[0057]

A relief pattern was engraved on the obtained printing element by a laser engraving apparatus (manufactured and sold by Baasel Lasertech), and the resultant was evaluated. The results are shown in Table 2 below.

The frequency of wiping needed to remove the debris (which is shown in Table 2 below) was defined as the number of times the wiping was performed to remove the viscous liquid debris generated during the laser engraving. A large frequency of wiping means that a large amount of liquid debris was present on the printing plate.

The number average molecular weight of the SBS (a thermoplastic elastomer) used in the Examples and Comparative Example was measured by gel permeation chromatography (GPC) using a calibration curve prepared using standard polystyrene samples. The number average molecular weight of the SBS was 77,000.

[0058]

Among the double bond-containing organic compounds used in the Examples and the Comparative Examples, BZMA, CHMA and PEMA are derivatives of an alicyclic compound or an aromatic compound. The softening temperature of the SBS used in the Examples and Comparative Examples was 130 °C as measured by a viscoelastic measurement apparatus, namely a rotary rheometer (manufactured and sold by Rheometrics Scientific FE, Ltd.). The softening temperature was measured under conditions wherein the test frequency was 10 rad/second and the temperature of a resin was elevated from room temperature at a rate of 10 °C/minute. The softening temperature is defined as the temperature at which the viscosity of the resin decreases drastically.

[0059]

[Example 5]

A photosensitive resin composition in a liquid state (trade name: APR,F320; manufactured and sold by Asahi Kasei Corporation) was shaped into a sheet having a thickness of 2 mm, and the shaped resin composition was photocured in the same manner as in Example 1, thereby obtaining a cushion layer of a printing element. On the above-obtained cushion layer was coated the photosensitive resin composition prepared in Example 4 so as to form a coating having a thickness of 0.8 mm. The photosensitive resin composition coating was subjected to an exposure process in the same manner as in Ex-

ample 1 to thereby obtain a printing element. The Shore A hardness of the cushion layer was 55.

A relief pattern was engraved using a carbon dioxide laser on the obtained printing element, and the resultant was evaluated. The relative amount of residual debris was 5.7 % by weight, the frequency of wiping needed to remove the debris was not more than 3 times and the tack on the printing element after wiping was 83 N/m. The portions of the relief pattern, which correspond to halftone dots, had an excellent cone shape.

[0060]

[Example 6]

100 Parts by weight of a polysulfone resin (trade name: Udel P-1700, manufactured and sold by Amoco Polymer) which is a non-elastomeric thermoplastic resin; 50 parts by weight of a double bond-containing organic compound used in Example 4; 5 parts by weight of an inorganic porous material (trade name: SYLOSPHERE C-1504, manufactured and sold by Fuji Silysia Chemical Ltd.); 0.6 part by weight of 2,2-dimethoxy-2-phenylacetophenone as a photopolymerization initiator; 0.5 part by weight of 2,6-di-t-butylacetophenone as an additive; and 50 parts by weight of tetrahydrofuran as a solvent were mixed together and stirred, thereby obtaining a photosensitive resin composition in a liquid state.

[0061]

A 50 μm -thick wholly aromatic polyamide film (trade name: Aramica; manufactured and sold by Asahi Kasei Corporation) which had been subjected to plasma treatment was coated with the above-obtained photosensitive resin composition in a liquid state so as to form a coating having a thickness of 1.5 mm. Since the photosensitive resin composition contained tetrahydrofuran (THF) as a solvent, the above-mentioned coating having a thickness of 1.5 mm was prepared by repeating a sequence of the coating and the subsequent drying under air for 3 times. The resultant was dried in a dryer to remove THF completely, thereby obtaining a shaped resin article. The shaped resin article was photocured by ALF type 213E exposure apparatus (manufactured and sold by Asahi Kasei Corporation). The exposure was performed for 10 minutes in vacuo, in which the upper surface of the sheet (on which a relief pattern was to be formed) was exposed at 2000 mJ/cm^2 and the other surface of the sheet was exposed at 1000 mJ/cm^2 , thereby obtaining a printing element.

[0062]

A relief pattern was engraved on the obtained printing element by a carbon dioxide laser engraving apparatus (trade name: TYP STAMPLAS SN 09; manufactured and sold by Baasel Lasertech), thereby obtaining a relief printing plate, and the obtained relief printing plate was evaluated. The relative amount of residual debris was 7.5 % by weight, the frequency

of wiping needed to remove the debris was not more than 3 times and the tack on the relief printing plate after wiping was 80 N/m. The portions of the relief pattern, which correspond to halftone dots, had an excellent cone shape.

The polysulfone resin used in Example 6 was in a solid state at 20 °C, and had a softening temperature of 190 °C as measured by a viscoelastic measurement apparatus, namely a rotary rheometer (manufactured and sold by Rheometrics Scientific FE, Ltd.). The softening temperature was measured under conditions wherein the test frequency was 10 rad/second and the temperature of a resin was elevated from room temperature at a rate of 10 °C/minute. The softening temperature is defined as the temperature at which the viscosity of the resin decreases drastically.

The number average molecular weight of the polysulfone resin used in Example 6 was 15,000 as measured by gel permeation chromatography (GPC), wherein a calibration curve prepared using standard polystyrene samples was used.

[0063]

[Example 7]

70 Parts by weight of a polysulfone resin (trade name: Udel P-1700; manufactured and sold by Amoco Polymer) which is a non-elastomeric thermoplastic resin; 30 parts by weight of a solvent-soluble polyimide resin (having a softening temperature of more than 500 °C); 50 parts by weight of a double

bond-containing organic compound used in Example 4; 5 parts by weight of inorganic porous material (trade name: SYLOSPHERE C-1504; manufactured and sold by Fuji Silysia Chemical Ltd.); 0.6 part by weight of 2,2-dimethoxy-2-phenylacetophenone as a photopolymerization initiator; 0.5 part by weight of 2,6-di-t-butylacetophenone as an additive; and 50 parts by weight of tetrahydrofuran as a solvent were mixed together and stirred, thereby obtaining a photosensitive resin composition in a liquid state.

[0064]

Using the obtained photosensitive resin composition, a printing plate was prepared in the same manner as in Example 6. A relief pattern was engraved on the obtained printing element by a carbon dioxide laser engraving apparatus (trade name: TYP STAMPLAS SN 09; manufactured and sold by Baasel Lasertech), thereby obtaining a relief printing plate, and the obtained relief printing plate was evaluated. The relative amount of residual debris was 7.5 % by weight, the frequency of wiping needed to remove the debris was not more than 3 times and the tack on the relief printing plate after wiping was 50 N/m. The portions of the relief pattern, which correspond to halftone dots, had an excellent cone shape.

[0065]

[Comparative Example 3]

A printing element was produced in substantially the

same manner as in Example 4 except that organic porous spherical particles were used instead of inorganic porous material. The organic porous spherical particles were cross-linked polystyrene particles having a number average particle diameter of 8 μm , a specific surface area of 200 m^2/g and an average pore diameter of 50 nm.

When a relief pattern was engraved using a carbon dioxide laser on the obtained printing element, a large amount of viscous liquid debris was generated and the frequency of wiping needed to remove the debris became more than 30 times. The reason for this is considered that the melting and decomposition of the organic porous spherical particles were caused by the laser irradiation and the organic porous spherical particles were unable to maintain the porous structure thereof.

[0066]

[Table 1]

	Resin (a)		Double bond -containing organic compound		Inorganic porous material		Polymeri- zation initiator		Other additives	
	Type	Amount	Type	Amount	Type	Amount	Type	Amount	Type	Amount
Ex. 1	SBS	100	BZMA	25	C-1504	5	DMPAP	0.6	BHT	0.5
			CHMA	19						
			BDEGMA	6						
Comp. Ex. 1	SBS	100	ditto		None		ditto		ditto	
Ex. 2	SBS	100	ditto		CH- 4004	5	ditto		ditto	
Ex. 3	SBS	100	ditto		C-470	5	ditto		ditto	
Ex. 4	SBS	100	LMA	6	C-1504	5	ditto		ditto	
			PPMA	15						
			DEEHEA	25						
			TEGDMA	2						
			TMPTMA	2						
Ex. 5	SBS	100	BZMA	25	C-1504	5	ditto		BHT	0.5
			CHMA	19					LB	5
			BDEGMA	6						
Comp. Ex. 2	SBS	100	ditto		Zeolite	5	ditto		BHT	0.5

Unit used to show the amounts of the components of the resin composition: parts by weight.

(Explanations of the abbreviations)

LMA : lauryl methacrylate (Mn: 254)

PPMA : polypropylene glycol monomethacrylate (Mn: 400)

DEEHEA : diethylene glycol-2-ethylhexylmethyl acrylate
(Mn: 286)

TEGDMA : tetraethylene glycol dimethacrylate (Mn: 330)

TMPTMA : trimethylol propane trimethacrylate (Mn: 339)

BZMA : benzyl methacrylate (Mn: 176)

CHMA : cyclohexyl methacrylate (Mn: 167)

BDEGMA : butoxy diethylene glycol methacrylate (Mn: 230)

PEMA : phenoxyethyl methacrylate (Mn: 206)
 DMPAP : 2,2-dimethoxy-2-phenylacetophenone
 BHT : 2,6-di-t-butylacetophenone
 LB : n-butyl laurate

(Additional Explanation): In the explanation above, the number shown after the term "Mn:" in the parentheses is the molecular weight.

[0067]

[Table 2]

	Relative amount of residual debris*1 (% by weight)	Frequency of wiping needed to remove the debris (BEMCOT impregnated with ethanol)	Tack on the relief printing plate after wiping (N/m)	Shape of relief portions corresponding to halftone dots
Ex. 1	8.0	≤ 3	55	Excellent cone shape
Comp. Ex. 1	12.5	30 <	180	Partially de-structed and slightly unclear halftone dots
Ex. 2	7.0	≤ 3	85	Excellent cone shape
Ex. 3	9.5	≤ 3	88	Excellent cone shape
Ex. 4	12.0	≤ 3	65	Excellent cone shape
Comp. Ex. 2	16.0	10	260	Excellent cone shape
Ex. 5	8.0	≤ 3	110	Excellent cone shape

*1) The relative amount of the residual debris =

$$\frac{[(\text{Weight of a printing element immediately after laser engraving}) - (\text{Weight of a relief printing plate after wiping})]}{[(\text{Weight of a printing element before laser engraving}) - (\text{Weight of a relief printing plate after wiping})]} \times 100$$

[0068]

[Effects of the Invention]

A printing element obtained by curing the photosensitive resin composition of the present invention not only generates only a small amount of debris during laser engraving and enables easy removal of the generated debris, but also is advantageous in that an excellent relief pattern can be formed on the printing element by laser engraving and the resultant image-bearing printing plate has small surface tack. As explained above, such a resin composition can be advantageously used in various fields.

[Name of Document] Abstract

[Abstract]

[Task] A task of the present invention is to provide a resin composition for forming a printing element which not only generates only a small amount of debris during the formation of a relief pattern directly on a printing element by laser engraving and enables an easy removal of the generated debris, but also is advantageous in that a precise image can be formed on the printing element by laser engraving and the resultant image-bearing printing plate has small surface tack.

[Means to Solve the Task] A photosensitive resin composition for forming a laser engravable printing element, comprising: (a) a resin which is in a solid state at 20 °C and having a number average molecular weight of from 5,000 to 300,000, (b) an organic compound having a number average molecular weight of less than 5,000 and having a polymerizable unsaturated group, and (c) an inorganic porous material having a specific surface area of from 10 m²/g to 1,500 m²/g, an average pore diameter of from 1 nm to 1,000 nm, a pore volume of from 0.1 ml/g to 10 ml/g and an oil absorption value of from 10 ml/100 g to 2,000 ml/100 g.

[Selected Figure] None

Historical Information on Applicant

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